

Enrichment of the amino acid L-isovaline by aqueous alteration on CI and CM meteorite parent bodies

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The distribution and enantiomeric composition of the 5-carbon (C₅) amino acids found in CI-, CM-, and CR-type carbonaceous meteorites were investigated by using liquid chromatography fluorescence detection/TOF-MS coupled with *o*-phthaldialdehyde/*N*-acetyl-L-cysteine derivatization. A large L-enantiomeric excess (ee) of the α -methyl amino acid isovaline was found in the CM meteorite Murchison ($L_{ee} = 18.5 \pm 2.6\%$) and the CI meteorite Orgueil ($L_{ee} = 15.2 \pm 4.0\%$). The measured value for Murchison is the largest enantiomeric excess in any meteorite reported to date, and the Orgueil measurement of an isovaline excess has not been reported previously for this or any CI meteorite. The L-isovaline enrichments in these two carbonaceous meteorites cannot be the result of interference from other C₅ amino acid isomers present in the samples, analytical biases, or terrestrial amino acid contamination. We observed no L-isovaline enrichment for the most primitive unaltered Antarctic CR meteorites EET 92042 and QUE 99177. These results are inconsistent with UV circularly polarized light as the primary mechanism for L-isovaline enrichment and indicate that amplification of a small initial isovaline asymmetry in Murchison and Orgueil occurred during an extended aqueous alteration phase on the meteorite parent bodies. The large asymmetry in isovaline and other α -dialkyl amino acids found in altered CI and CM meteorites suggests that amino acids delivered by asteroids, comets, and their fragments would have biased the Earth's prebiotic organic inventory with left-handed molecules before the origin of life.

enantiomeric excess | homochirality | origin of life | carbonaceous chondrite

Meteorites provide a record of the chemical processes that occurred in the early solar system before life began on the Earth. In particular, the carbonaceous chondrites are carbon-rich meteorites with up to 2 wt % organic carbon (1). The delivery of organic compounds by carbonaceous chondrites to the early Earth could have been an important source of the Earth's prebiotic organic inventory (2). The amino acid composition of carbonaceous meteorites has been characterized extensively because these prebiotic molecules are the monomers of proteins and enzymes in all life on Earth. Over 80 different amino acids have been identified in the CM meteorites Murchison and Murray, and they comprise a mixture of 2- to 8-carbon cyclic and acyclic monoamino alkanolic and alkanedioic acids of nearly complete structural diversity, many of which are completely nonexistent in the terrestrial biosphere (1, 3–5). In addition, many amino acids are structurally chiral. With a few very rare exceptions, only left-handed amino acids (L) are found in biology, whereas all known abiotic syntheses of amino acids result in equal mixtures of left- and right-handed ($L \approx D$) amino acids. The origin of “homochirality” has been investigated for well over a century since Louis Pasteur discovered chirality, and it continues to be a topic of great importance in the origin of life field. There appear to be no biochemical reasons why left-handed amino acids should be favored over right-handed amino acids in enzymes (6), and therefore some have argued that the selection of left-handed amino acid homochirality by life on Earth was a random process (7).

The finding of slight to significant enantiomeric excess (ee) for several indigenous amino acids in the Murchison and Murray

CM2-type meteorites could point toward a possible prebiotic contribution to the origin of biological homochirality by the delivery of extraterrestrial organic material from asteroids and comets to the early Earth. These analyses showed enantiomeric excesses of the left-handed form (L_{ee}) ranging from 0% to 15.2% for isovaline and enantiomeric enrichments for several other α -methyl amino acids, including α -methylnorleucine, α -methylvaline, α -methylnorvaline, α -methylisoleucine, and 2-amino-2,3-dimethylpentanoic acid (8–11). Pizzarello et al. (11) also found a possible correlation between the magnitude of the L-isovaline excesses observed in individual fragments of the Murchison meteorite and the relative abundance of hydrous silicate minerals, hinting that aqueous alteration may have played a role in amino acid asymmetry in this meteorite. These α -methyl amino acids are nonbiological, and unlike the α -hydrogen amino acids used in biochemistry, they are not prone to geologically rapid racemization under aqueous or radiogenic conditions (12). Therefore, the initial enantiomeric ratios of these α -methyl amino acids are much more likely to have been preserved since the time of their formation.

The enantiomeric measurements of α -methyl amino acids in Murchison and Murray reported by Pizzarello and co-workers were made by using a gas chromatography/mass spectrometry (GCMS) technique, and great care was taken to rule out all potential sources of error. Nevertheless, to date these results have not been independently confirmed by using a different analytical technique. Moreover, very few meteorites have been investigated for isovaline asymmetry. To further constrain enantiomeric excesses in CM carbonaceous meteorites and to investigate the possibility that aqueous alteration on the parent body may have contributed to amplification of amino acid asymmetry, we reinvestigated the Murchison meteorite by using the very sensitive and selective liquid chromatography fluorescence detection (LC-FD)/TOF-MS technique that we optimized for the separation and enantiomeric determination of the 5-carbon (C₅) amino alkanolic acids, including isovaline. We also report here the results of analyses of C₅ amino acids in the aqueous altered CI1 meteorite Orgueil, the less altered Antarctic CM2 meteorite Lewis Cliffs (LEW) 90500, ungrouped C2 meteorite Lonewolf Nunataks (LON) 94102, and the most pristine Antarctic CR2 meteorites Elephant Moraine (EET) 92042 and Queen Alexandra Range (QUE) 99177.

Results and Discussion

Amino Acid Analyses. Examination of the exact mass chromatogram of the acid-hydrolyzed, hot-water extracts of the carbonaceous meteorites by LC-FD/TOF-MS shows the C₅ α -, β -, γ , and δ -amino alkanolic acid isomers that eluted in the 20- to 45-min region [Fig. 1 and supporting information (SI) Fig. S1]. All identified peaks were confirmed by comparison with standards, fluorescence, and

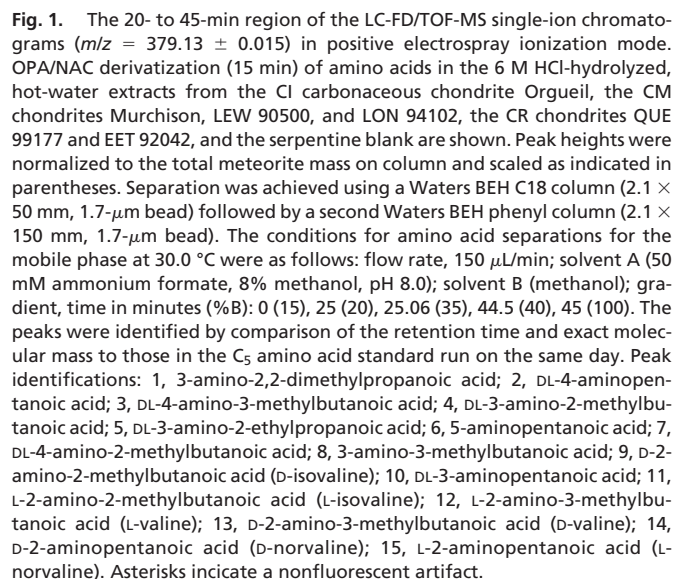
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The CR chondrites are believed to contain the most primitive organic material of any carbonaceous chondrite group (21, 22), and it has recently been discovered that two Antarctic CR2 meteorites, EET 92042 and Graves Nunataks (GRA) 95229, have the highest total amino acid concentrations (180,000 and 249,000 ppb, respectively) in any meteorite reported to date, with isovaline concentrations ranging from 23,000 to 29,000 ppb (23). However, the more altered CR1 meteorite Grosvenor Mountains (GRO) 95577 had a much lower total amino acid abundance of ≈ 900 ppb (23), suggesting that some of the amino acids or their precursors were destroyed or leached from this meteorite during aqueous alteration.

chiral β - and γ -amino isomers because these amino acid enantiomers were not separated or optically pure standards were not available for their identification. We observed very low D/L ratios for isovaline in Murchison (0.69 ± 0.04) and Orgueil (0.73 ± 0.07), which correspond to L-isovaline excesses of $18.5 \pm 2.4\%$ for Murchison and $15.2 \pm 4.0\%$ for Orgueil (Table 1). The Murchison value measured in this study exceeds the highest value of 15.2% previously measured for Murchison (11). The L-isovaline excess measured in Orgueil has not previously been reported in this or any CI meteorite and is similar to the Murchison value within error. Because isovaline is highly resistant to racemization (12), the measured D/L ratios should not have increased since the time of formation. Some radioracemization ($\approx 5\%$) of isovaline could have occurred based on the expected ionizing radiation dose from radioactive decay inside the Murchison and Orgueil meteorite parent bodies (24). However, radioracemization would only act to decrease the isovaline excesses observed in these meteorites; therefore, the values measured in this study should be considered lower limits for the initial L-isovaline excess.

Another possibility is enhancement of the L-isovaline excess in meteorites by terrestrial L-amino acid contamination after their fall; however, isovaline is a nonprotein amino acid that is extremely rare on the Earth, is found predominately in its D configuration in fungal peptides (25) and was not identified above the 10 ppb detection limit in a soil sample collected from the Murchison meteorite fall site (26). Furthermore, carbon isotopic measurements of D- and L-isovaline in Murchison did not display any significant difference in their $^{12}\text{C}/^{13}\text{C}$ ratios, which would have been detected if significant terrestrial contamination of one of the enantiomers had occurred (11). We were unable to make carbon isotope measurements of isovaline in Orgueil given the extremely low concentrations (≈ 85 ppb) and limited meteorite sample available for analysis. The finding of large L-isovaline excesses in Murchison and Orgueil suggests that enantiomeric enrichment occurs after the formation of this amino acid in the meteorite parent body because the most plausible ketone precursor for the synthesis of isovaline (2-butanone) is achiral, and laboratory abiotic simulations of the Strecker–cyanohydrin synthesis produce racemic mixtures of α -amino and α -dialkyl amino acids (27, 28). The formation of isovaline by the Strecker synthesis in Murchison is supported further by the detection of the α -hydroxy acid (α -hydroxy- α -methyl butyric acid) predicted to form by the Strecker mechanism from the same chemical precursors as isovaline (29). The enantiomeric ratio of α -hydroxy- α -methyl butyric acid is currently unknown, and it cannot be detected by the OPA/NAC derivatization technique used in this study.

With the exception of Orgueil and LON 94102, the D/L ratio of the protein amino acid valine in the other meteorites was nearly racemic (Table 1 and Table S1), indicating that very little terrestrial L-amino acid contamination occurred in these samples. Assuming that the extraterrestrial D/L valine ratios in Orgueil and LON 94102 were racemic, as found for the other meteorites, the currently measured D/L values of 0.39 ± 0.10 for Orgueil and 0.74 ± 0.05 for LON 94102 suggest that some terrestrial L-valine amino acid contamination of these meteorites occurred after their fall to Earth. The Orgueil meteorite fell in France in 1864, and its varying levels of contamination are well known. In contrast to valine, the non-protein amino acids isovaline and norvaline are much less abundant in the terrestrial biosphere and are therefore unlikely amino acid contaminants. We found that, for all of the carbonaceous meteorites analyzed, the D/L ratio of norvaline was racemic (≈ 1.0) within experimental error (Table 1 and Table S1), providing additional evidence that this nonprotein amino acid is extraterrestrial in origin. Because of the lack of pure standards, the individual D- and L-enantiomers of 3-apa were not identified. However, the meteoritic 3-apa appears to be as racemic as the commercial DL standard. We cannot rule out the possibility that these chiral C_5 amino acids had L-enantiomeric excesses at the time of formation. However,

these C_5 amino acids are not resistant to racemization; therefore, any initial enantiomeric excess could have been rapidly eliminated during periods of aqueous alteration on the meteorite parent body.

The measured D/L ratios for isovaline in the CR meteorites QUE 99177 and EET 92042 were racemic within measurement uncertainty, $\text{D/L} = 0.99 \pm 0.04$ and 1.02 ± 0.08 , respectively (Table S1). Although D/L isovaline ratios for these two CR meteorites have not previously been reported, amino acid enantiomeric measurements for another Antarctic CR meteorite, GRA 95229, using GCMS also showed low L-isovaline excesses of $\approx 3\%$ (22). In the same meteorite, Pizzarello et al. (22) found that the C_6 amino acid diastereomers L-isoleucine and D-alloisoleucine had enantiomeric enrichments of $\approx 12\text{--}14\%$, which was similar to the chiral distribution of these amino acids found in the more altered meteorite Murchison. If one invokes the Strecker–cyanohydrin synthesis, then the asymmetries in isoleucine and alloisoleucine in GRA 95229 and Murchison possibly were derived from asymmetry in their C_5 aldehyde precursor (22); however, isovaline would not likely have obtained its asymmetry by the same mechanism because 2-butanone is achiral. These observations suggest that the chemical processes and environments that led to the asymmetry in isovaline in Murchison were different from those for the aldehyde precursors that led to the asymmetry in isoleucine and alloisoleucine. The large L-isovaline excesses in Murchison and Orgueil and apparent lack of L-isovaline excesses in pristine CR2 meteorites indicate that aqueous alteration was an important process for isovaline enantioenrichment on the CM2 and CI1 parent bodies.

Amplification of Amino Acid Asymmetry During Aqueous Alteration.

On the basis of mineralogical and chemical evidence, in situ aqueous alteration was an important process on the CM meteorite parent body, with liquid water timescale estimates ranging from 10^2 to 10^4 years (30, 31). Aqueous alteration of the CM meteorites is believed to have been the result of the melting of ice inside the asteroid by radioactive heating, largely by the short-lived radionuclides ^{26}Al and ^{60}Fe (17, 32). The CI meteorites also experienced alteration, as demonstrated by their high abundance of hydrated minerals, oxygen isotope values, and high water-to-rock ratio compared with those of other groups of carbonaceous meteorites (33, 34). Although it has been suggested that the CI meteorites could be fragments of comets or extinct cometary nuclei (35, 36), the idea that liquid water was present in the interior of comets has been controversial, with some models suggesting that it is unlikely (37). The primitive nature of the insoluble organic matter found in Antarctic CR meteorites compared with that of CI and CM meteorites (38) suggests that some CR meteorites experienced only minimal aqueous alteration and thermal metamorphism. However, we should emphasize that even meteorites within the same class show evidence for various degrees of aqueous alteration and thermal metamorphism (38).

In addition to changing the mineralogy and volatile contents, aqueous alteration can also modify the soluble organic composition. It has been observed that the relative distribution of amino acids in carbonaceous chondrites is influenced by the degree of aqueous alteration on the parent body (13). In general, the more altered meteorites have a higher relative abundance of the amino acid β -alanine, whereas meteorites experiencing a lower degree of alteration have a much higher relative abundance of AIB. The variation in $\beta\text{-Ala}/\text{AIB}$ ratios follows a consistent trend with aqueous alteration, and this pattern was observed for the meteorites analyzed in this study (Fig. 3). In fact, the least altered CM meteorite, Yamato 791198, analyzed to date (39) has the highest relative abundance of AIB (40). A similar trend was previously observed in several Antarctic CR meteorites, where the least altered CR2 meteorites EET 92042 and GRA 95229 exhibit higher relative abundances of AIB, whereas the more altered CR1 meteorite GRO 95577 has a higher relative abundance of β -alanine (23).

The D/L ratios of chiral amino acids in meteorites have not been

(150 °C for 1 week). Enantiomerically pure samples of 4-a-2-mba were also supplied by R. Duke (University of Sydney, Sydney, Australia).

Meteorite Samples and Processing Procedures. All glassware and sample handling tools used for the meteorite samples were rinsed with Millipore water, wrapped in aluminum foil, and then heated in an oven at 500 °C overnight. Several fragments of the Murchison meteorite (6.3 g obtained from the Smithsonian National Museum of Natural History, USNM 6650,2), an interior chip of the Orgueil meteorite (1.0 g from the Musée National, Paris), the Antarctic meteorites LEW 90500 (5.0 g, split 69, parent 1), LON 94102 (0.6 g, split 19, parent 7), QUE 99177 (0.5 g, split 29, parent 10), and EET 92042 (0.6 g, split 58, parent 0) provided by the Antarctic meteorite curator at the National Aeronautics and Space Administration Johnson Space Center were crushed separately into fine powders and homogenized by using a mortar and pestle in a positive pressure high-efficiency particulate air-filtered laminar flow bench. As controls, a sample of serpentine (a hydrated magnesium silicate mineral common in carbonaceous meteorites) that had been heated at 500 °C for 3 h and standard mix of C₅ amino acids were carried through the identical procedure as the meteorites.

A portion of each sample (~100–200 mg) was sealed separately in a glass ampoule with 1 mL of Millipore water and extracted at 100 °C for 24 h, and the water supernatants were subjected to a 6 M HCl acid vapor hydrolysis procedure

(150 °C for 3 h). The acid-hydrolyzed, hot-water extracts were desalted by using cation-exchange resin (AG50W-X8, 100–200 mesh, hydrogen form, Bio-Rad), and the amino acids were recovered by elution with 2 M NH₄OH (prepared from NH₃(g) (Air Products and Chemicals) in vacuo). The amino acids in the NH₄OH eluates were derivatized with OPA/NAC followed by positive electrospray ionization LC-FD/TOF-MS (Waters ACQUITY UltraPerformance LC and Waters LCT Premier) or LC-QqQ-MS (Waters Quattro micro API). The C₅ amino alkanolic acids and their enantiomeric ratios in the meteorite extracts were then quantified from the peak areas generated from the exact mass chromatogram of their OPA/NAC derivatives (379.1328 Da) from a minimum of 8 separate analyses. A more detailed description of the processing procedures, analytical technique, and quantification method is provided elsewhere (13).

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